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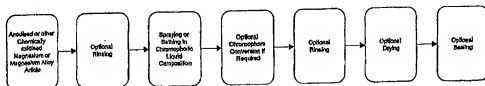
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(54) Title: **COLOURING MAGNESIUM OR MAGNESIUM ALLOY ARTICLES**



(57) Abstract

A method of colouring a magnesium or magnesium alloy article which involves immersion or spray contacting an anodized or other oxidized surface of the article with at least one species of chromophoric moiety in a liquid carrier in conditions which maintain the integrity of said anodized or other oxidized surface yet which results in the chromophore(s) becoming associated (directly or via a moiety or species attached to the chromophore) with the surface by a reaction or adsorption. The species is preferably selected from the group consisting of reactive dyes, direct dyes, VAT dyes, sulphur and disperse dyes.

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"COLOURING MAGNESIUM OR MAGNESIUM ALLOY ARTICLES"

Introduction

The present invention relates to a method of colouring magnesium or magnesium alloy material having an anodized or other oxidised surface (as in the chemical meaning, ie; a transfer to a higher oxidation state, not limited to magnesium oxide) of the magnesium or magnesium alloy and to the product of such a process and related apparatus and procedures. The present invention also consists in a related procedure for increasing corrosion resistance.

The colouring of magnesium alloy articles that have been anodized (or otherwise chemically oxidised) has defeated most attempts by experimenters attempting to provide a range such as is available for anodized aluminium. Whereas the colouring of anodized aluminium is available through several methods, there are no simple analogies available for magnesium even though much research has been directed towards this goal over a period of some years.

As most anodic films generated on aluminium have a regular hexagonal pore structure, characterised by the spacing, size and even distribution of the pores, several options for colouring aluminium involve inducing colouring agents (dyes, metal ions or pigments) to enter the pores. Once the colouring step has concluded, the article is generally "sealed", a treatment that closes the pores and in effect, locks the colouring material into place. Transition metal ions achieve a strong colouring effect when used in this manner.

Magnesium anodic films feature a pore structure as well, but unlike aluminium this is not well characterised and the pores are unevenly distributed. The pores range in diameter, but are generally larger than the aluminium pores. Also, the anodic film is translucent or opaque, not transparent, therefore any colouring effect from a species introduced into a pore may be more limited.

Nonetheless, early experimenters attempting to produce a range of colours on anodized magnesium articles tried to use aluminium colouring systems. These were completely unsuccessful. One reason is that most aluminium colouring systems operate under conditions of acid pH at which aluminium is relatively impervious to dissolution.

Magnesium does not exhibit the amphoteric behaviour of aluminium, which is usually anodized under acid conditions, and most magnesium anodising processes are alkaline. Acid processes applied to magnesium articles normally result in rapid dissolution of the metal, with the exception of a few acids which form insoluble magnesium compounds that cover and passivate the metal.

Acid colouring systems are therefore usually inapplicable to magnesium and will ordinarily result in attack of the substrate metal as well as the anodic film. As one of the principal reasons for anodising the metal is to increase corrosion resistance, using a colouring process that attacks the substrate or anodic film is contra-indicated.

Even if a method of introducing transition metal ions into anodic film pores was developed it is unlikely to be satisfactory. This is because magnesium is a highly reactive metal, considerably more so than aluminium, and the presence of such species at the base of the film pores would introduce micro galvanic cells ready to initiate corrosion. As corrosion resistance may be a reason for anodising magnesium substrates an increase in the corrosion susceptibility of the substrate is not usually commercially acceptable.

US Patent 4,551,211 (Ube Industries) discloses a method of anodising a magnesium article in a solution containing very high concentrations of aluminium (as aluminate ion) resulting in a combined magnesium/aluminium oxide matrix which can then be coloured using conventional aluminium dyeing technology. The process is notable for its difficulties in application and expensive chemicals being required (iodides). The colouring method there disclosed cannot be extended to other anodic films. US Patent 4,551,211 admits to the complexity of the process.

Other attempts at colouring have resulted in a loss in corrosion resistance. An example is the MAGOXID™ process described in US Patent 4,978,432 (Schmeling). This teaches a method of anodising magnesium in which the formation of phosphate and aluminate salts of magnesium is preferred above the oxide. A licensee of this Magoxid process, Luke Engineering of Ohio report in their process literature that:

"Some progress is being made in coloring this coating. Currently, however, significant reduction in corrosion resistance is an unwanted side effect of dyeing."

"Operations in Magnesium Finishing", of the Dow Chemical Company, (1990)

includes the statement:

"Anodizing of magnesium essentially follows the same procedure used on other metals: soil removal, deoxidation and anodisation. Both alkaline and acid anodizes are available. Unlike such coatings on aluminium, however, anodic coatings on magnesium do not lend themselves to dyeing. For colour effects on magnesium, clear anodizes or bright pickles are used in combination with tinted or dip-dyed clear lacquers."

5 Until the present invention there has been no elegant answer to a desire to colour magnesium. Thus far prior art processes that have achieved limited success have done so at the expense of some other desirable property. We believe there are several reasons
10 why this should be so. Whilst we theorise in this respect hereinafter we do so on a without prejudice basis to the invention hereinafter defined.

The present invention is directed to a method of colouring magnesium or magnesium alloys which provides a material having a coloured yet protection providing anodized or other oxidised surface. By the term "other oxidised surface" is not meant
15 a modification of the surface with an oxidised metal of a different species as in US Patent 4,551,211.

It is also the object of the present invention to provide products modified by a method of the present invention and related methods and means.

In a first aspect the present invention consists in a method of colouring a
20 **magnesium or magnesium alloy article**, said method comprising or including the steps of ensuring the article has, or providing the article with an anodized or other oxidised surface of the magnesium or magnesium alloy, and

contacting said anodized or other oxidised surface with at least one species of chromophoric moiety in a liquid carrier in conditions, or in a sequence of conditions,
25 not substantially prejudicial to the integrity of said anodized or other oxidised surface yet which results in the chromophore(s) becoming associated (directly or via a moiety or species attached to the chromophore) with the surface by a reaction or adsorption.

Preferably said conditions exclude the prospect of an aluminium build up on said surface even should the magnesium have been alloyed with aluminium.

30 Preferably the carrier is aqueous.

Preferably said surface is anodized.

In some forms of the invention said surface is chemically oxidised.

Preferably the conditions include elevated temperature(s).

Preferably the step of contacting is by immersion although spraying is another option to find favour.

Preferably the method includes washing the anodized or other oxidised surface
5 prior to contact with said at least one species of chromophoric moiety in a liquid carrier.

Preferably the method includes a washing step subsequent to the contact with said at least one chromophoric moiety in a liquid carrier.

Preferably said conditions involves a near neutral, neutral or alkaline pH.

Preferably said pH is alkaline or at least as alkaline as the dye process will allow.

10 Preferably said species is selected from the group consisting of reactive dyes, direct dyes, VAT dyes, sulphur dyes and disperse dyes (as defined in the Colour Index).

Most preferably the species is one of the group consisting of reactive dyes, VAT dyes and sulphur dyes.

Preferably said species is selected from the group consisting of vinyl sulphones,
15 monochloro triazines, dichloro triazines, pyrimidines, phthalocyanines, quinoxalines, aniline derivatives, monofluoro triazines, anthraquinones, indigo and halogenated indigo derivatives, polysulphides, and diazo phenols.

Preferably said species is selected from the group consisting of vinyl sulphones, monochloro triazines, dichloro triazines, pyrimidines, phthalocyanines, quinoxalines,
20 monofluoro triazines, anthraquinones, indigo and halogenated indigo derivatives, polysulphides, and diazo phenols.

In another aspect the invention comprises or includes

- (i) providing a bath containing a sulphur textile dye together with alkali and a reducing agent such that the dye is present in its water-soluble reduced leuco
25 form;
- (ii) immersing said article in said bath; and
- (iii) subsequently immersing said article in an oxidising solution to form the dye on its surface.

Preferably said bath is at approximately 90°C for approximately ½ an hour.

30 Preferably said sulphur textile dye is provided at approximately double the normal concentration employed for textile dyeing.

In still another aspect the invention comprises or includes

- (i) providing a bath containing a VAT textile dye together with an alkali and reducing agent such that the dye is present in its water soluble leuco form;
- (ii) immersing said article in said bath; and
- 5 (iii) immersing said article in a mildly acidic oxidising solution to form the dye on the surface of the article.

Preferably said reducing agent is sodium dithionite.

Preferably said article is immersed at approximately 70 °C for approximately 30 minutes.

- 10 Preferably said VAT textile dye is provided at double the normal concentration employed for textile dyeing.

Preferably said article is immersed in said mildly acidic oxidising solution for approximately five minutes.

In yet another aspect the invention comprises or includes

- 15 (i) providing a bath containing a vinyl sulphone reactive textile dye;
- (ii) immersing said article in said bath; and
- (iii) washing said article.

Preferably said bath is provided at a pH of approximately 12 and said article is immersed for approximately 30 minutes at at least 60 °C (preferably 80 °C),

- 20 Preferably said bath contains a reactive dye, and at least one of sodium carbonate, sodium hydroxide or sodium silicate.

Preferably said bath contains a reactive dye in a concentration of 5g/L and sodium carbonate, also at a concentration of 5g/L and sodium hydroxide at a sufficient concentration to raise the pH to about 12.

- 25 Preferably said washing is in water at at least 60 °C (preferable with a wetting agent, eg; ethylene glycol).

In yet another aspect the invention comprises or includes

- (i) providing a bath containing a monochloro triazine reactive textile dye;
- (ii) immersing said article in said bath; and
- 30 (iii) washing said article.

Preferably said bath and said article is immersed for approximately 30 minutes

at approximately 60°C.

Preferably said bath contains a reactive dye, and at least one of sodium sulphate, sodium chloride, carbonate and sodium hydroxide.

Preferably said bath comprises a reactive dye in a concentration of 0.5 - 2% and
5 Na_2SO_4 concentration is equal to dye concentration, sodium carbonate 0.5 - 1% and NaOH 0.25%.

Preferably said washing is in water at 80°C.

In one embodiment of the invention said surface is anodized and said at least one species of chromophoric moiety in a liquid carrier is a reactive dye of a kind having a
10 vinyl sulphone functional group and wherein the conditions are within a temperature range of from 30 to 100°C during an immersion or spray presentation of the liquid dye composition to the anodized surface for at least 10 minutes and thereafter a rinsing step with water at an elevated temperature.

Preferably said contact time is about 30 minutes.

15 Preferably said rinsing step is with hot water containing a wetting agent and the temperature of the aqueous rinsing composition is 80°C or greater.

Preferably said temperature of the immersion or spraying with the liquid dye composition is at about 60°C.

20 Preferably the dye has a concentration of at least about 0.5% w/v in an aqueous system.

In another embodiment of the invention said surface is anodized and wherein the at least one species of chromophoric moiety in a liquid carrier is a reactive dye of a kind having a monochloro triazine functional group and the conditions during the contact by immersion or spraying is contact at an elevated temperature.

25 Preferably the contact time is for a period of from 30 to 60 minutes.

Preferably the elevated temperature of the contact is at about 70°C or higher.

Preferably the dye concentration is from 0.5% to 2% w/v.

Preferably there is also present sodium sulphate at substantially equal concentration to the dye, sodium carbonate at 0.5 to 1.0% w/v and sodium hydroxide
30 to a concentration of about 0.25% w/v.

Preferably there is a rinsing step with hot water containing a wetting agent and

at a temperature of 80°C or greater.

In another embodiment of the invention said at least one species of chromophoric moiety in a liquid carrier is that of a reactive dye having a dichloro triazine functional group or a monofluoro or difluoro triazine functional group.

- 5 Preferably the conditions are similar to those for monochloro triazine functional groups.

In still another embodiment the at least one species of chromophoric moiety in a liquid carrier is a reactive dye of the pyrimidine type.

- 10 In a different embodiment the at least one species of chromophoric moiety in a liquid carrier is that of a vat dye.

Preferably the dye is an anthraquinone or indigo derivative.

Preferably the vat dye is dispersed in water and reduced to water soluble leuco form using a combination of a reducing agent and alkali.

- 15 Preferably said leuco dye is used to colour anodized magnesium article by immersion or spraying.

Preferably the temperature of leuco dye is elevated. Most preferable 60°C or higher.

Preferably pH of leuco dye is 11.5 or greater.

- 20 Preferably leuco dye dyed article is rinsed in cold water (eg; 5 seconds) and then oxidised so that leuco dye is converted to insoluble pigment.

In another embodiment the at least one species of chromophoric moiety in a liquid carrier is that of a sulphur dye.

Preferably the moiety is attached to a polysulphide.

- 25 Preferably the sulphur dye is dispersed in water and reduced to water soluble leuco form (thiol form) using a combination of a reducing agent and alkali.

Preferably said leuco dye is used to colour anodized magnesium article by immersion or spraying.

Preferably the temperature of leuco dye is elevated. Most preferable 60°C or higher.

- 30 Preferably pH of leuco dye is 11.5 or greater.

Preferably leuco dye dyed article is rinsed in cold water (eg; 5 seconds) and then

oxidised so that leuco dye is converted to insoluble pigment.

In still another embodiment the at least one species of chromophoric moiety in a liquid carrier is a direct dye.

Preferably said direct dye comprises a chromophoric moiety attached to a sodium
5 sulphonate group.

Preferably direct dye is present in solution 0.5 to 2% w/v with sodium sulphate 0.5 to 2% w/v and, optionally, sodium carbonate to a concentration of about 0.25 to 1% w/v.

Optionally an anodic potential of approximate 10 to 20 V DC may be applied to
10 the anodized article.

Preferably temperature of dye solution is at least 60°C.

Preferably dyed article is rinsed after dyeing.

In yet another embodiment the at least one species of chromophoric moiety in a liquid carrier is a disperse dye.

15 Preferably dye is evenly dispersed in water to the extent of at least 0.25% w/v.

Preferably a carrier being an ester is added to aid dyeing.

Preferably the article is introduced into the dye dispersion at 100°C or greater (eg; under pressure) and maintained in such contact for 20 to 90 minutes.

Preferably the article is subsequently rinsed.

20 In still a further aspect the present invention consists in a method of increasing the corrosion resistance of an anodized magnesium or magnesium alloy surface which comprises the step of colouring such a surface by a process as previously defined

Preferably the at least one species of chromophoric moiety in liquid carrier is that of a reactive dye of a kind having a vinyl sulphone functional group.

25 In some forms of the present invention the at least one species of chromophoric moiety in a liquid carrier is an acid dye using an acid which forms magnesium salts.

Preferably said acid is lactic acid.

Optionally the contact step with the liquid carried chromophoric moiety or moieties is a multiple step process. Such multiple step process may result from multiple

30 dipping, sequential spraying or a hybrid of dipping and spraying.

Optionally a plurality of compatible chromophoric moieties are used such as

might result from mixed dyes.

In a further aspect the present invention consists in a **magnesium or magnesium alloy material** having a coloured anodized or other oxidised surface, said colouring having been achieved using a method in accordance with the present invention.

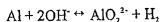
5 Preferred forms of the present invention will now be described.

Figure 1 is a simple flow diagram showing the optional steps sometimes preferred.

Preferred surfaces to be coloured include those anodized by a process such as disclosed in PCT/NZ96/00016 (WO 96/28591) (Barton) or as disclosed in our PCT
10 International Application filed simultaneously herewith.

We believe (without wishing to be bound to such a theory) that historically attempts to anodize magnesium have been made under the shadow of already known aluminium techniques and it has been presumed that the technologies applicable to aluminium can be modified in some way to make them work on magnesium.

15 However, this approach we believe to be flawed. The metals aluminium and magnesium are fundamentally different. Aluminium is amphoteric and is usually anodized in acidic media. In solutions of strong alkalis, the metal dissolves releasing hydrogen:



20 Magnesium does not react with strong alkalis, and magnesium oxide is insoluble in bases such as sodium hydroxide whereas aluminium oxide is readily soluble in such bases.

The oxidation of aluminium results in a well-defined surface oxide layer which features regular hexagonal pores having a diameter of about $0.1\mu\text{m}$. These result from
25 the dissolution of the anodic film in the electrolyte in which it is partially and slowly soluble. Magnesium forms pores as well, but not because of any solubility of the anodic film in its electrolytes. In alkaline electrolytes it appears that the film is insoluble. In such acidic electrolytes as are used it may be slightly soluble but it is only with the presence of added species that an impervious barrier film results. For example
30 anodisation of magnesium may be conducted in acid fluoride solutions in which an

impervious layer of magnesium fluoride results.

The anodic film formed on aluminium is transparent in thin films and colours resulting from pigments or dyes deep within the pores therefore impart an overall colour to the film. Aluminium dye systems cannot be applied directly to magnesium anodic
5 films.

Films formed on magnesium substrates are not transparent and have a natural colour. This is sometimes slightly off-white, but can be quite dark, depending on the electrolyte and conditions of anodisation. Colouring such a film would not be a simple matter of introducing a dye into the pores, which in any case are irregular and typically
10 have diameters ranging from $2\mu\text{m}$ to $5\mu\text{m}$.

A colorant suitable for use on magnesium therefore has to mask whatever natural colour the surface has in addition to providing a strongly adherent layer itself. It is almost inevitable that any suitable method for colouring magnesium will add another layer to the surface owing to the translucent nature of the coating.

15 Some conversion coatings are available for use on magnesium substrates and these produce, in some instances, strongly coloured substrates. For instance, British Patent 493,935 describes a method by which a chromate or permanganate conversion coating may be formed on a magnesium article. The coatings formed by this method are typically very dark and even black. Such is not considered "colouring" for the present
20 purpose as the colour cannot be controlled and the coating formed is not a true anodic film. The process cannot be applied to an anodic film or an already existing other oxidised coating. As transition metal compounds such as permanganate or chromate are present the corrosion resistance rendered by these processes may be reduced owing to micro-galvanic cell formation.

25 One class of aluminium dyes comprises inorganic compounds that result from a two-step process in which an insoluble colour is precipitated in the second stage of the process. The first stage introduces a water-soluble species to the pores in the aluminium oxide anodic film. This species is adsorbed onto the surface of the anodic film. The diffusion of these species into the pores in the anodic film is governed by the surface
30 charge on the film, known as the *zeta potential*. Ordinarily this is positive, but in suitable electrolytes it may be changed.

Double dip processes only work in the correct sequence. Thus for instance, in producing a bronze colour by this method using cobalt acetate and potassium permanganate, it is necessary to dip the aluminium article into the cobalt acetate solution first. It is believed that if the permanganate is used first, potassium cations are

5 adsorbed preferentially leaving no permanganate ions available for reaction with the cobalt acetate.

Examples of binary inorganic salt pairs that may be used to colour an anodic coating on aluminium include:

- | | | |
|----|--|---------------|
| 10 | • Cobalt acetate/potassium permanganate | Bronze |
| | • Ferric ammonium oxalate/potassium ferrocyanide | Blue |
| | • Ferric ammonium oxalate/tannic acid | Black |
| | • Copper sulphate/ammonium sulphide | Green |
| | • Lead nitrate/potassium chromate | Yellow |
| 15 | • Ferric sulphate/potassium ferrocyanide | Prussian blue |

This process is specific to aluminium as the adsorption of the soluble species occurs inside the pores and relies on the surface chemistry and charge of the aluminium oxide anodic film. Consequently, a parallel process involving inorganic ions does not

20 exist for magnesium anodic films.

Organic colouring may also be employed on aluminium, although in most cases the dyes are adsorbed rather than undergoing a chemical reaction with the substrate. Acid and substantive dyestuffs normally react with the substrate but on aluminium anodic films they do not, although a colour is produced. The colour is not particularly

25 wash or light fast.

In cases where there is a true chemical reaction the result is a light fast colour. Dyes of the metal complexing acid colour type come into this category. These appear to form new complexes with aluminium atoms.

There are also single dip inorganic baths which colour aluminium. It is believed

30 that the pigments are adsorbed directly into the pores. These processes tend to be very sensitive to pH.

Two points are evident in connection with the use of these agents on magnesium:

1. The dyes that work on aluminium are acid based and will usually have an adverse effect on the anodic film produced on magnesium.
2. Precipitating inorganic compounds inside the pores will not be effective on magnesium due to the translucent nature of the film.

Accordingly, the use of aluminium dyes to colour magnesium is not effective except in the special case described above where the anodic film is modified to have a very high content of aluminium oxide (US Patent 4,551,211).

10 Dyes for alkaline conditions

We believe that since magnesium is best anodized under alkaline conditions a suitable colouring technology should also operate under conditions of alkaline pH. Such a technology would have to provide effective bonding between the magnesium oxide substrate and good colour fastness.

- 15 An extensive range of dyes and colouring chemicals is available world-wide yet, these have been designed for specific applications.

The range of existing colouring compounds includes simple pigments, such as titanium dioxide, which is used very widely as a brilliant white colour in paints, and exotic chemically-formed dyes which are the basis of photography.

- 20 In this discussion, a "pigment" may be regarded as being a coloured molecule which is insoluble and unreactive. A pigment may colour an article by virtue of being in close contact with it although usually a carrier is required to ensure that it stays in place. For example, titanium dioxide is chemically inert and insoluble in aqueous solution or solvents. It is dispersed in paints and forms an opaque, brilliantly white layer
- 25 when applied to articles in suspension in suitable carriers. Insolubility alone does not result in a pigment, as some insoluble colouring compounds may still react chemically with the substrate.

- A "dye" on the other hand is often soluble in its carrier and in many cases it is chemically reactive with the substrate to which it will bond. In some cases, the
- 30 "reaction" may be the formation of a clathrate compound, hydrogen bond or Van der Waals bond, while in others it may be a true chemical reaction.

There is overlap between pigments and dyes, because in some cases, a colouring agent is initially a dye, but is converted to a pigment once it has penetrated the substrate that is to be coloured. In some cases, a pigment is converted to a soluble, reactive form, which is then a dye, after application of which, it is converted back to a pigment.

- 5 We have determined that some colouring compounds designed for textile applications have application in colouring magnesium anodic films. In most cases optimisation of the process has required alterations to conditions of application and the use. In some cases we have found an anodic or cathodic potential may be applied to the magnesium article. Such a potential is not applied to any textile material for use with
- 10 the same dye systems. Also, there is no simple parallel to the fibre penetration processes that are usually part of the mechanism by which a textile fibre adsorbs dye molecules. In many cases where alkaline textile dyes are employed, sodium hydroxide present in the dye bath assists in penetration of the fibre because it promotes softening and swelling of the fibre. The most applicable dyes are those applied to cellulosic fibres,
- 15 such as cotton. The cotton fibre consists of a central core of polyhydric alcohols surrounded by inert cellulose.

An anodic magnesium substrate has no such compounds on its surface and is completely inorganic in composition.

- The exact chemical composition of an anodic film produced on magnesium
- 20 depends on the process being employed, but there are some common general features.

Typically, the electric fields employed in anodising magnesium are very high, resulting in deprotonation of the forming film and therefore the formation of magnesium oxide, rather than magnesium hydroxide. Ordinarily the oxide ion, O^{2-} , is instantly hydrolysed in aqueous solution:



In the case of anodisation of magnesium, the electric fields are often in the region of 1×10^9 volts per metre, sufficient to ensure the presence of oxide ions at active reaction sites.

- The generic processes widely employed to "anodize" magnesium are based on
- 30 electrolytes containing sodium hydroxide and additives, or an acid fluoride salt plus

additives. Typically these processes produce a rough, porous, partially sintered anodic film comprising magnesium oxide together with included species. On the surface, owing to hydrolysis, some magnesium hydroxide is formed.

Specialised processes are often designed to produce other species, or to include species that are present in the electrolyte. Such species may include silicates or borates. The process described in US Patent 4,978,432, mentioned above, is designed to ensure cationic species are available at reaction sites with the intention that magnesium phosphate and magnesium aluminate be formed. Even so, it is expected that magnesium oxide and hydroxide will feature as part of the film as well.

The process disclosed in PCT NZ96/00016 (WO 96/28591) also creates an anodic film comprising principally magnesium oxide, with some surface magnesium hydroxide formation, but it does this in a manner which leads to less sintering of the coating and more uniform distribution of pores.

Clearly anodized metal substrates are unlike the surfaces normally coloured using fibre-penetrating textile dyes.

Despite these differences, we have determined that certain classes of compounds described in the Colour Index and intended for textile application can be applied to anodized magnesium substrates resulting in satisfactory colours. Amongst these are the following classes of compounds, although there are others that work as well:

Vinyl sulphones, Monochloro triazines, Dichloro triazines, Pyrimidines, Phthalocyanines, Quinoxalines, Aniline derivatives, Monofluoro triazines, Anthraquinones, Indigo and halogenated indigo derivatives, Polysulphides, and Diazo phenols.

Commonly, these dyes comprise a *chromophore* which is a functional group which is attached to a reactive group that may bond either chemically or physically to the substrate. Since the same chromophore may be used in dyes that react differently to form the final coloured article, there is considerable overlap in the functional groups and a consideration of each class of reactive group is required. A good example of chromophore overlap is in the area of turquoise dyes. Most turquoise dyes are based on phthalocyanine, which can form a range of blue and green hues when appropriately substituted, but will not readily form other colours. This chromophore is widely used

to produce turquoise shades in reactive dyes and direct dyes, as well as other classes where appropriate.

Within classes of compounds, dyes may be mixed to obtain colours different from those of the individual compounds. When mixing of dyes is carried out it must be borne in mind that the most effective mixing strategies are those which mix similar types of chromophores as well as reactive groups. Accordingly, while it is possible to mix a vinyl sulphone reactive dye with a monochloro triazine reactive dye, the results that are obtained may not be as expected owing to differences in reactivity. Also, even if, for instance, two vinyl sulphone reactive dyes are mixed, the result may not be the intermediate colour expected as the chromophores may not be compatible. Very often, for any given set of dyes, there is a trichromic set specified which are three dyes, most commonly a yellow, blue and red dye, from which it is possible to generate a wide range of intermediate colours as these dyes are able to be mixed in all proportions without ill effect.

Also, in some circumstances, it may be desirable to double or multiple dip a magnesium article in a second dye after completing a process in a first dye. Provided there are no fundamental chemical incompatibilities between stages, this is possible and could commonly be employed to produce the corrosion resistant substrate that results from infusion with a reactive dye, but to use a more light fast dye to colour the article. The hydrogen bonding of direct and vat dyes is not usually affected by a process involving a reactive dye as a first step and in some cases when not all reactive sites have been chemically bonded to a reactive dye, it is possible to double dip an article in a second reactive dye.

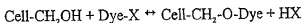
Dyeing an article that has been anodised may also be conducted for the reason of increasing the salt spray resistance of the article and not for any specific colour requirement in the final product. In tests it has been found that the salt spray resistance of anodised magnesium test plates has been considerably enhanced when those test plates have been coloured. Improvements of 100% in salt spray resistance may be obtained in some circumstances, thereby justifying the colouring of anodised articles for this reason alone.

Reactive Dyes

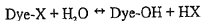
These compounds are so named because normally there is a true chemical reaction between the dye molecule and the substrate. A considerable range of reactive dyes may be found listed in the Colour Index, but new compounds are continually being synthesised. In a cellulose molecule, there are secondary hydroxyl molecules attached to the ring:



The reactive dye bridges the oxygen by the following reaction:

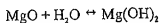


- 10 The result is a strongly adherent, chemically bonded colour that exhibits a high degree of wash-fastness. However, an alternative and undesired side reaction also takes place:



- 15 This hydrolysis of the dye proceeds more rapidly under alkaline conditions, which unfortunately, are also the very conditions which are required to activate and catalyse the dyeing reaction. Since hydrolysed dye is normally poorly adherent, it must be rinsed out thoroughly after dyeing. Most reactive dyes have low substantivity so that hydrolysed dye may be removed from dyed articles easily. The hydrolysis of the dye has the effect of lowering the pH of the dye bath.

- 20 Since an anodic film on a magnesium substrate comprises essentially magnesium oxide, it would not ordinarily be expected that such a dye would work well on magnesium. However, some surface hydrolysis of the magnesium oxide is favoured thermodynamically:



- 25 The dye may therefore react with the magnesium hydroxide bridging an oxygen atom as happens in the cellulose molecule. Since the magnesium hydroxide is formed on the surface, this form of dyeing would meet the requirements of the foregoing discussion.

Application of a reactive dye to a magnesium anodic film is conducted in a

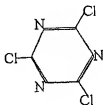
solution containing reactive dye, and a base, at a bare minimum. Often additional alkali, and sometimes an ionic salt can improve the dye exhaustion. The dyeing reaction is more active under more alkaline conditions and the presence of salt may help aggregate the dye on the substrate surface owing to the common ion effect. The reaction normally
5 takes place at a temperature of around 60°C and sometimes higher.

Under some circumstances, the dyeing reaction can be influenced favourably by applying an electric charge to the surface of the magnesium oxide. This can be done easily by means of the electrolytic apparatus used to anodize the substrate.

Hydrolysed dye is unavoidably present in the dye bath and some of this would
10 diffuse into the pores of the magnesium article and adhere weakly to the surface. It seems that long after a reactive dye would be regarded by the textile industry as unsuitable for use owing to the extensively hydrolysed nature of the dye molecules, it is still possible to dye anodic films on magnesium. Often there is a slight shift in the shade obtained, presumably because the hydrolysed dye cannot bond chemically to the
15 substrate and must be physically adsorbed.

Although it appears that hydrolysed dye may still provide satisfactory colouring, it is normal after dyeing to have to rinse well in hot aqueous solutions containing a wetting agent, to remove quantities of unreacted and poorly adherent dye as otherwise drying marks will affect the finish of the magnesium article.

The functional groups present in a reactive dye are normally vinyl sulphone or
20 derivatives of trichloro triazine (cyanuric trichloride), such as monochloro triazine. Some reactive dyes comprise two or more reactive groups. In cases where two reactive groups are present, a benefit may accrue from combining, for example, a vinyl sulphone with a monochloro triazine group. If one group is hydrolysed, the dye may still bond
25 chemically to the substrate.



Reactive dyes have to be small molecules so as to penetrate the cellulose fibre thus enabling the reaction. This generally means one chromophore only, and this should most advantageously be a small group, for instance a monoazo or diazo compound. Often a reactive dye will have the following structure:

5

Chromophore-NH-(Reactive group)

Sometimes it is possible to produce intermediate colours by attaching a second chromophore to a reactive dye, but in such cases the molecule is generally too large to function properly as a reactive dye. An example is CI Direct Green 26, in which the molecule is based on a reactive dye, but contains two chromophores, a yellow and a blue, attached to a molecule of cyanuric trichloride.

To colour an anodized magnesium article in a reactive dye we recommend the following steps be carried out:

- 15 1. Article thoroughly rinsed following anodising process, especially if process is an acid-fluoride process.
 2. Prepare reactive dye by heating deionised water bath to around 60°-80°C.
 3. Add salt (if required), base (such as sodium carbonate, if required) and alkali (such as sodium hydroxide, if required).
 - 20 4. Add dye and mix well to ensure complete dissolution.
 5. Introduce article to be coloured and maintain temperature. Most reactive dyeing processes will require 20-60 minutes.
 6. Rinse article in hot water, preferably 85°C or higher, containing a wetting agent such as ethylene glycol, maintaining article in rinse bath for at least two minutes.
 - 25 7. Repeat step #6 until all residues of poorly adherent hydrolysed dye are removed.
- If the rinsing process is not carried out correctly, hydrolysed dye will leach from areas that are drying leaving drying marks on coloured articles. If necessary, such marks may be removed by re-rinsing in very hot or even boiling water. Concentrations of reactive dyes used to colour magnesium are often greater than those employed on textile materials. There is no need to use auxiliaries which for textile application are present to aid in fibre penetration.
- 30

It is common for reactive dyes for textile application to be applied progressively in a dye bath to which the dye is added, then after a period of time, salt and alkali. Such a method does not appear to be beneficial when dyeing magnesium substrates.

5 Reactive Dyes (Most Preferred Conditions):

(a) Vinyl sulphone functional group dyes.

- * Relatively thick anodic film (15 microns plus)
 - * Temperature at 60°C
 - * Dye concentration 0.5%
 - 10 * Sodium carbonate concentration 0.5%
 - * Sodium hydroxide to adjust pH of 1% dye bath solution to 11.5 - typically this is around 0.25% concentration
 - * Dyeing time at least 10 minutes. Preferably about 30 minutes
 - * Rinse step, highly preferred - hot water containing a wetting agent such as
 - 15 ethylene glycol 0.1%, most preferably 80°C (or greater) for one minute or longer.
- Preferably the article is a temperature where it will quickly dry and there will be no leaching of hydrolysed dye.

(b) Monochloro triazine functional groups:

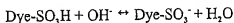
- 20 * Anodic film 15 microns or greater most preferred
- * Dye concentration 0.5% to 2%
- * Sodium sulphate concentration 0.5% to 2%, equal to dye concentration
- * Sodium carbonate 1%
- * Sodium hydroxide 0.25%
- 25 * Temperature -- most preferably 70°C (the process probably works quite well at any temperature above this, but fairly slowly at lower temperatures)
- * Time - at least 10 minutes - 30-60 minutes is typical

- (c) Other types of reactives - conditions most favourable to our applications are similar to those above e.g. a dichloro triazine dye requires similar temperatures and
- 30 concentrations to a monochloro triazine dye. Pyrimidine based reactive can also be used.

Direct Dyes

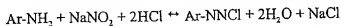
Compounds described in the Colour Index as *direct dyes* bond to cellulosic fibres by way of secondary chemical bonds, such as hydrogen bonds or van der Waals forces. As these bonds are not as strong as true chemical bonds, the molecules are designed to be large, thereby strengthening the bond. Most direct dyes range in molecular weight from 400 to 1,200. Most direct dyes are azo dyes, and possess a linear structure.

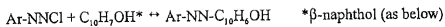
Direct dyes must be soluble in water. Generally in practice, a direct dye is applied to a cellulosic fibre by means of an aqueous solution in which a soluble ionic salt, commonly sodium sulphate or sodium chloride is dissolved. The ionic salt assists in the dyeing process as it is believed that it aids in the charge transfer between the dye and the fibre, thus enhancing dye uptake by the fibre. Often direct dyes contain sodium sulphonate groups. These ensure high water solubility and enable the dye molecule to form an ionic aqueous solution under conditions of alkaline pH:



As the dye chromophore is negatively charged, it is attracted to any ions that are positively charged and repelled from negatively charged ions or surfaces. The addition of an ionic salt is thought to assist in dyeing partly because of the "common ion" theory in which the dye is "salted out" or aggregates are formed. As there is a balance between water solubility and affinity for the substrate, a balance between exhaustion of the dye onto the substrate and that remaining in solution is established. The more alkaline the pH, the greater the water solubility of the dye. After a point, it also increases the affinity of the dye for the aqueous phase, rather than the insoluble fibre, hence it reduces exhaustion of the dye.

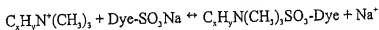
It is possible in some cases to improve the fastness of the dyed article by after processing the dyed article to render the dye in an insoluble form. This may be done by increasing the size of the molecule. Direct dyes which contain a primary amino group attached to an aromatic ring may be diazotised and coupled to a naphthol component. This process tends to alter the dye colour as an azo group is added:





5

Cationic agents, comprising a long chain hydrocarbon tertiary amine may be added to improve wash-fastness:



10

The resulting organic molecule is very large and not soluble in water. Such agents added to an aqueous solution of a direct dye will cause the precipitation of the dye.

In the case of magnesium, the dye may have affinity for the layer of hydroxide formed at the surface of the anodic film, the bonding that results being hydrogen bonding similar to that existing in water.

15

Application of a direct dye to a magnesium article may involve a solution being made comprising the direct dye, a salt (commonly sodium sulphate) and in some cases, sodium carbonate or other suitable base. The use of sodium sulphate is preferred over the use of sodium chloride as chloride ions are noted as initiators of pitting corrosion and are therefore an unwanted species inside the pores of the anodic film. The dye is normally heated to around 70°C, although in some cases higher temperatures may be desired.

20

The dyeing is normally complete after 60 minutes.

Since the soluble dye molecule tends to be negatively charged when the sodium sulphonate group dissociates, an anodic voltage applied to the dye bath can improve dye deposition substantially. Such a voltage is ordinarily fairly low but depends on the thickness of the anodic film as this is an efficient insulator. Voltages less than 50 volts are normal.

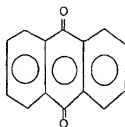
25

Direct Dyes (Most Preferred Conditions)

- * Prepare dye bath at a concentration ranging from 0.5% to 2% w/v
- * Add sodium sulphate at similar concentration; viz 0.5% to 2% w/v
- * Add sodium carbonate, 0.5% w/v, especially to direct black dyes
- 5 * Heat to 60°C and immerse article for 60 minutes
- * Optionally, apply an anodic voltage to the part in the order of 10V.
- * Remove, rinse and dry.

VAT Dyes

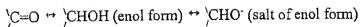
- 10 Vat dyes are in fact insoluble pigments that are reduced to a water soluble *leuco* form in alkaline conditions for application to a fabric or anodized magnesium article, prior to being converted back to an insoluble pigment that is then highly light and wash fast on the finished article. According, the vat "dye" as such has a transitory existence in the leuco form. Vat dyes are described in the Colour Index under the heading "Vat
- 15 Dyes". Most are based on 9,10 anthraquinone, which of itself is colourless. However, once azo or other chromophores are attached to the ring structure, a wide range of colours may be obtained.



- 20 Vat dyes include *indigo*, a substance originally of natural origin, which is not light fast, but which over time fades gradually in successive washes and is favoured for
- 25 denim to create the characteristic "faded denim" look. Indigo and a few halogenated derivatives are still in use, although only indigo and tetrabromoindigo are of commercial importance currently.

There are also fused ring polycyclic compounds that form good vat dyes.

- 30 Vat dyes are characterised by the presence of a keto group which can be reduced to an alcohol. This may then form a salt under conditions of alkaline pH:



The "salt" of the enol form is the leuco vat dye. This is water soluble and is therefore a true dye, rather than a pigment whereas the keto form is insoluble and is
5 classed as a pigment.

It is believed that vat dyes form hydrogen bonds to magnesium hydroxide molecules, thereby forming a dyed surface. To dye an anodized magnesium or magnesium alloy article with a vat dye we recommend the following steps:

1. Dispersion of the dye in water. This must be done evenly, without the formation
10 of lumps. Generally anthraquinone and other vat dyes are now available with a particle size of less than $1\mu\text{m}$, enabling an even dispersion in water to be made.
2. Reduction - while various agents may be used, the most common in dyeing textiles is sodium dithionite, usually known as sodium hydrosulphite. This produces the enol form of the dye. Sodium dithionite gives satisfactory results
15 when the dye is to be used on magnesium substrates.
3. Adsorption of the dye - in alkaline solutions, the leuco vat dye is adsorbed onto the surface of the magnesium article, forming an evenly coloured surface. Excessive quantities of undissolved pigment present in the solution may result in "bronzing" of the surface so this should be avoided.
- 20 4. Oxidation of the reduced dye, once it has formed a layer on the substrate, may be conducted by an oxidising bath or simply by sufficient exposure to air. Suitable oxidising baths comprise hydrogen peroxide or sodium perborate solutions, but alternatives including dichromates may be used. The optimum oxidising bath is acidified to a pH of 5-6 using acetic acid. It should be noted
25 that the colour of the reduced leuco form of the dye may not be identical to the insoluble pigment form and thus to some extent the final shade obtained may depend on the oxidant used. An example of this is CI Vat Green 9, which is a very dark olive green as oxidised by air or hydrogen peroxide. However, it can be oxidised in stronger oxidants to a neutral shade of black.
- 30 5. Rinsing to remove any excess dye follows oxidation and in most cases there is a rinse stage between dye adsorption and oxidation to remove excess reducing

agent and alkali, in addition to any unadsorbed dye.

The procedure must be carefully balanced for excessive reduction may result in reduction of the enol form of the dye and therefore a loss of shade and fastness. Some vat dyes are affected by light in the leuco form, while others are precipitated by calcium ions in the water supply. Deionised water should be used for preparation of vat dyes. Anodized magnesium substrates must be very carefully rinsed prior to introduction to the bath containing the reduced leuco dye as free magnesium ions may also precipitate an insoluble compound from the dye bath.

10 Vat Dyes (Most Preferred Conditions):

All vat dyes have some common features regardless of whether the dye is a indigoid or anthraquinone type.

For a few black vat dyes the oxidation procedure is slightly different because of the difficulties inherent in achieving black through dye systems. A chromophore molecule possesses a colour, as viewed under white light because of the absorbance of certain portions of the visible light spectrum by the molecule. True black requires the absorption of all of the visible light spectrum. Since this ideal case is not in practice readily obtainable, the most common procedure is to take a very dark colour and apply it in a manner intended to generate such a dark tone that it appears black. This may be done in a few instances by a more aggressive oxidation of the leuco dye. CI Vat Green 9, as referred to above, may be made to appear black in this manner whereas it is normally a dusky olive green shade. It is more difficult to achieve this result on a magnesium anodic film substrate than on a cellulosic textile substrate and it is thus not part of the preferred procedure, nor are the oxidants (chrome VI) commonly employed for this purpose regarded as satisfactory for application generally.

Common features:

Preparing vat stock solution:

- * Heat deionised water to 85°C
- * Add 100g/litre of dye (as supplied, the dye is actually a pigment, comprising the water insoluble keto form of the dye)

- * Add 250ml/litre of 10 molar sodium hydroxide solution (400g/litre)
 - * Mix thoroughly, then add:
 - * 100g/litre sodium dithionite
 - * Agitate at 85°C for fifteen minutes then cool and hold in dark, stoppered flask
- 5 (this is necessary because the solution will absorb oxygen from the air and denature otherwise; also some leuco vat dyes are light-sensitive).

To "vat" the dye, ready for use:

- * Deionised water at 60°C -- 800ml/litre (ie: to make 10 litres of dye, start with 8
- 10 litres of deionised water)
- * Add 10ml/litre of 10M sodium hydroxide
 - * Add 5g/litre sodium dithionite
 - * Add 100ml/litre stock dye solution
- 15 Make up to full volume with deionised water and dye parts to be coloured at 60°C or greater for 30 minutes.
- * After dyeing, rinse in cold water for 5 seconds
 - * After rinsing, oxidise in a solution containing sodium perborate (15.4 grams/litre) or hydrogen peroxide (0.5%) or a mixture, adjusted most preferably with acetic acid to a pH of approx 5, for five minutes.
- 20 * Remove, rinse and dry.

Instead of oxidising in hydrogen peroxide/sodium perborate, the article may be oxidised in air (but the full oxidation process takes several days) or other oxidants. Sodium or potassium dichromate, acidified with acetic acid is quite effective.

- 25 The vat dyes may be operated at a higher concentration than this - these figures were intended for textiles. We found that a better shade resulted from doubling the concentration (this meant using 200ml/litre stock solution instead of 100ml/litre).

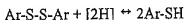
- Vat dyes do not last in air because of the absorption of atmospheric oxygen and the downward drift of pH which should remain above 12. The pH drift is due to the acids released by the sodium dithionite as it reduces the keto pigment to the enol form.
- 30 If extra sodium dithionite has to be added, sodium hydroxide must be added with it, in a ratio of 1.2 parts sodium hydroxide to 1 part of sodium dithionite.

Sulphur Dyes

Sulphur dyes offer only a limited range of colours, none of them bright, because of the large size of the complex polysulphide rings formed, but they are fast and economical to apply to magnesium substrates. They are described in the Colour Index.

- 5 Like vat dyes, sulphur dyes are in fact finely dispersed pigments which must be reduced to a soluble form in order for dyeing to proceed satisfactorily. After dyeing, the dye is oxidised back to the insoluble form, either by air or by an oxidising solution containing a suitable agent, often hydrogen peroxide or sodium perborate in aqueous solution.

- A sulphur dye is normally a disulphide, which may be reduced to a thiol. The
10 exact chemistry of a sulphur dye is still not fully understood, but the reduction reaction proceeds:



- The leuco form of the sulphur dye is applied to the article in aqueous solution at elevated temperatures, often around 80 °C, in the presence of an ionic salt, often sodium
15 chloride or sodium sulphate, which assists the exhaustion of the dye.

- The reducing agent for the dye may be sodium dithionite but there are also proprietary agents available. Glyceraldehyde, hydroxyacetone, certain sugars, and various other agents are commonly found constituents of such reducing agents. Some proprietary reducing agents also contain alkalis, as these are also required to generate
20 the soluble leuco form of the dye. This limits the requirement to add alkali separately to the bath.

Alkali is also required to enhance the solubility of the thiol. In commercial applications, sodium hydroxide is normally used although other alkalis serve equally well.

- 25 One problem in connection with sulphur dyes is that some dye decomposition may take place on the finished article. This results in the liberation of acid residues that may damage a magnesium part. For this reason, a finish in a mildly alkaline oxidising bath, rather than an acid solution is advised.

- To dye an anodized magnesium article using a sulphur dye we recommend the
30 following steps:

1. Anodized article rinsed thoroughly
2. Sulphur dye bath made up and heated to around 90°C. Dye bath contains an ionic salt, sodium sulphate being preferred, although sodium chloride may also be used*. Reducing agent is added to form the leuco dye. If sodium dithionite is used, sodium hydroxide or another base should be added as the reduction process generates acid, lowering the pH.
3. Maintain the dye bath at 90°C for 30 minutes with the magnesium article present.
4. Wash off excess dye.
5. Oxidise the dye to the insoluble pigment form, either by atmospheric oxidation (which takes several days to go to completion) or by using agents such as hydrogen peroxide or dichromate solutions. As is the case with vat dyes, the nature of the oxidant used can affect the final shade of the dye and the leuco dye may not be the same colour as the insoluble pigment formed upon oxidation.

15

SULPHUR DYES (Preferred Conditions)

The sulphur dyes work much the same way as the vats, except the complex polysulphide rings are actually split into two by the reducing action of the reducing agent which is then soluble in alkali. The most favoured procedure, at the moment, is:

20

- * Start with 800ml deionised water at 40°C
- * Add 80ml/litre of sulphur dye suspension (CI Leuco Sulphur Dye Black 1 is sold as an aqueous suspension of the pigment).
- * Add 80ml/litre of Reducer NS™ a proprietary alkaline reducing formulation.
- 25 * Add 1 g/litre sodium hydroxide
- * Agitate for ten minutes then heat to 85°C
- * At 85°C, add 60 g/litre sodium chloride or sodium sulphate over ten minutes. Raise temperature to 95°C.
- * Introduce article to be coloured and hold at this temperature for 30 minutes.
- 30 * Rinse in cold water for five seconds
- * Oxidise using hydrogen peroxide/sodium perborate solution as per vat dyes for

twenty minutes at 50°C. As for vat dyes, various oxidants may be used.

One problem with sulphur dyes is that there is a tendency for the dyes to release acid upon decomposition, which is a negative feature for this will attack the anodic film. We therefore recommend not making the oxidising bath acidic in order to maintain an alkaline surface on the magnesium anodic film.

Disperse Dyes

The Colour Index lists a number of compounds where the chromophore is bonded to an intentionally insoluble compound to create a dye, which is applied as a finely dispersed suspension to dye certain types of fibres, such as polyesters. These dyes are thought to be solubilised either to a very slight extent either by a carrier, which is added to the bath, or at the surface of the fibre. The dissolved dye molecule can then migrate into the fibre. Monoazo and anthraquinone disperse dyes are common, but a range of varieties exist including diazo, nitrodiphenyl, methane, styryl, benzodifuranone and quinophthalone compounds. Carriers such as chlorobenzenes or aromatic esters increase the affinity of the substrate for the dye.

Since these compounds work by intermolecular penetration into textile fibres, it is not obvious why they dye magnesium anodic films although these films are not simple compounds such as magnesium oxide as a variety of species is present and there is some hydration at the surface. It is known that staining sometimes occurs with disperse dyes and this may result in quite a wash resistant colour, hence it may be that the bond between the anodic film and the dye is more of the nature of a stain. This does not of itself imply that the coloured article is unsuitable for general application. It is believed that these dyes enter and plug up pores in the anodic film thereby imparting a colouring effect.

Disperse Dyes (Most Preferred Conditions)

- * Make up dye dispersion in water to required strength 0.5% to 2%
- * Add carrier (generally an aromatic ester), 2%, to dye bath
- * Heat to boil and introduce article for 30-60 minutes.
- * Remove, wash and dry

Other Dyes

In addition to the categories listed above it is possible to obtain satisfactory colours on magnesium anodic or oxidised film substrates using some other dyes.

- Acid dyes normally attack both the substrate and anodic film, a clearly unsatisfactory result. However, by substituting lactic acid or similar organic acid which forms an insoluble magnesium salt, for acetic acid in the general formulation it is possible to obtain a less aggressive formulation which can, for very short immersions or spray contact times, result in a stain that may be regarded as satisfactory colouration. To conduct this procedure would entail:

- 10 *
- * Lactic acid -- 1-2%
- * Acid dye -- 0.5-2%
- * Optionally sodium sulphate 0.5-2%
- * Heat dye bath to 60 C or greater
- 15 *
- * Immerse magnesium article for short period, ideally shorter than 2 minutes
- * Wash thoroughly

- A uniform stain may result without any significant surface or substrate degradation. However a longer immersion may result in a loss of the anodic or oxide film and attack of the substrate.

AZOIC DYES

- These are really a special category of direct dyes in which the adsorbed species is colourless until diazotised by the procedure described on pages 19 and 20. The diazotisation creates the required colour. Generally these dyes are naphthol or phthalocyanine based. The intermediates involved in this process include relatively unstable diazonium compounds thus this procedure is quite sensitive to environmental fluctuations.

- It is best to use these dyes at very low temperatures, around freezing point. The optimal procedure involves:

- 30 *
- * Introduce magnesium article to colourless coupling component in solution in

bath. The coupling component is often a derivative of 3-hydroxy-2-naphthoic acid. Heat bath to elevated temperature, 70 C or greater.

- * Optionally salt (sodium sulphate) may be added to improve uptake of coupler.
- * In separate vessel, prepare diazonium salt. While this is best stabilised as the hydrochloride salt, it is preferable to avoid mineral acids because of their tendency to attack the substrate.
- * Remove article from coupling agent and immerse it in diazonium salt bath.

The coloured dye will be formed inside the anodic film.

10

Application to anodized magnesium

Clearly, the ability to colour an anodized magnesium article is a considerable advantage when such methods are not generally available, or are highly process-specific and awkward to apply. The dyes and methods of application outlined above are generally applicable to magnesium anodising processes, including that outlined in PCT NZ96/00016 (WO 96/28591) and the prior art processes known as "TAGNITE™", "MAGOXID™", "DOW 17™" and "HAET™".

The MAGOXID™ process is disclosed in US Patent 4,978,432. TAGNITE™ is described in the Society of Automotive Engineers (SAE) Aerospace specification AMS#2467 and US Patent 5,470,664.

TAGNITE™ is a "spark" anodisation process characterised by the presence of plasma discharges all over the surface of the part during the process.

"MAGOXID™" is intended to produce a layer comprising magnesium aluminate and magnesium phosphate, using a pulsed or AC current to achieve cationic presence near the substrate surface. It is described in US Patent 4,978,432 and has been referred to herein above.

DOW 17™ is an acid fluoride based anodisation process that produces an intrinsic green film whose colour intensity depends on the end point voltage of the process. In some cases it may be very dark. Clearly the reason why such a film would be coloured would not normally be to produce a range of colours as the intrinsic substrate colour limits this, but to benefit from the improved corrosion resistance

30

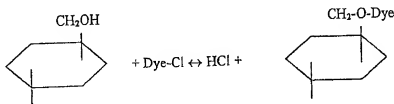
imparted by colouring. DOW 17™ colours well in these dyes although its intrinsic colour limits the range of shades obtainable.

HAE™ is an alkaline anodising process using an alkali hydroxide, potassium fluoride, trisodium phosphate and potassium manganate in solution. It produces varying shades of brown coating which is not intrinsically amenable to taking a colour, but which may be coloured using the dyes described herein to take advantage of the improvements in salt spray corrosion resistance obtained in doing this.

It is our understanding that these colouring processes require the presence of magnesium hydroxide, at least in so far as reactive dyes are concerned, to form a true chemical bond with the substrate. While not wishing to be confined to that theory, it is our supposition that there would be surface deposits of magnesium hydroxide, formed by hydrolysis of the magnesium oxide anodic film, on the surfaces of parts anodized using either TAGNITE™ or the process described within PCT NZ96/00016 (WO 96/28591). Furthermore, we believe that MAGOXID™ also produces such a surface, even though the inventors have sought to form other species within the film.

The colouring processes described herein are applicable to all film thicknesses although optimum results are obtained on thicker films.

The reactive dyes will selectively split a secondary hydroxyl group in a cellulose molecule, as pictured below:



25 It is our understanding (although we do not wish to be so bound) that the reactive groups within the dye molecules will cleave the magnesium hydroxide molecule in a similar way, bridging the remaining oxygen atom to form a true chemical compound.

The other dyes, which do not necessarily form a true chemical compound, are believed to bond to magnesium hydroxide in much the same manner as they do to a cellulose fibre inside a cellulosic fibre, such as cotton. Therefore, hydrogen bonding and van der Waals forces are presumed to exist between molecules of magnesium hydroxide

30

and the dyes, just as they do within the fibre.

If a colour is applied incorrectly, or the wrong shade results, it is possible to strip the dye from the surface either progressively or completely to enable recolouration. Methods of stripping are mostly simple, for instance, by immersion in solutions of lactic acid, which does not adversely affect the substrate.

As used herein percentages where the context allows are expressed as weight to volume.

EXAMPLES

10 - Example 1

A direct black dye was used to colour a 10 micron anodic film on magnesium alloy AZ91D: a 0.5% solution of Ciba-Geigy's Solophenyl® Direct Black GN dye was prepared and heated to 60°C. 0.5% sodium sulphate by weight was added and an anodic voltage of 10 volts was applied to the article. After 30 minutes the article was found to be a deep black in colour.

- Example 2

A second article was introduced to the dye bath outlined in example #1 above, but no anodic voltage was applied to it. After 60 minutes it was found to be a charcoal grey in tone.

- Example 3

A strip of hot rolled anodized AZ31 magnesium alloy, having an anodic film of 15µm was introduced to a dye bath containing a monochloro triazine reactive blue dye which was freshly prepared. The bath contained:

- (a) 1% dye (Ciba Geigy's Cibacron® Blue HGN)
- (b) 1% sodium sulphate
- (c) 0.5% sodium hydroxide
- (d) 1% sodium carbonate

The dye bath was heated to 70°C and the sample held for twenty minutes. At the end of the time, the article was found to be a deep and uniform blue in colour.

Hydrolysed dye was rinsed from the article which was then allowed to dry naturally in air.

- **Example 4**

- 5 A die casting composed of AZ91D magnesium alloy was coloured black using CI Leuco Sulphur Dye Black 1, a liquid dispersion of sulphur dye. The sulphur dye was converted to the soluble leuco form by adding a proprietary reducing agent, Reducer NS and salt as follows:

- (a) CI Leuco Sulphur Dye Black 1 - 8%
- 10 (b) Reducer NS - 8%
- (c) Sodium chloride - 80 grams per litre

- The solution was heated to 90°C and the magnesium article introduced to the bath for thirty minutes after which it had an even flat black appearance. Finishing comprised a rinse in hot water then an oxidising bath comprising hydrogen peroxide, 15 0.5% and sodium perborate 10 grams per litre. This bath was heated to 40°C. After this treatment, the article was dried and when dry, had a uniform flat black appearance.

- **Example 5**

- A die cast component comprising AZ91D magnesium alloy was coloured in a 20 vat black dye using sodium dithionite as a reducing agent and sodium hydroxide as an alkali. The leuco dye was prepared in the following manner:

- A stock vat dye dispersion was prepared from 100 grams per litre vat dye and 250ml per litre 10 molar sodium hydroxide solution. To this was added 100 grams per litre of sodium dithionite to solubilise the dye, converting the dispersion to the water 25 soluble enol salt form.

This stock dye was then added to deionised water at 60°C in the following proportions:

- | | |
|--------------------------------------|-------------------|
| Deionised water | 900ml per litre |
| Sodium hydroxide solution (10 molar) | 10ml per litre |
| 30 Sodium dithionite | 5 grams per litre |
| Stock solution (as described) | 100ml per litre |

This solution of leuco dye was maintained at 60°C and the anodized part was introduced to it. It was coloured a charcoal grey shade which did not visibly change as the dyed part was rinsed and oxidised in a solution of 0.5% hydrogen peroxide and 14 grams per litre sodium perborate.

5

- **Example 6**

A strip of hot rolled AZ31 magnesium alloy was introduced to a suspension of a disperse dye, CI Disperse Red 1 to which had been added 0.1% Pecar® GL, a proprietary carbonyl acid ester carrier compound. The dye bath was heated to boiling
10 point and maintained for 30 minutes after which time the magnesium article was found to be a pastel orange-pink colour.

- **Example 7**

A number of magnesium alloy AZ91D test plates were anodised to a nominal
15 film thickness of 20 microns using the process described in PCT/NZ96/00016. A number of these were coloured using several different vinyl sulphone reactive dyes, whereas the remainder were not coloured.

These samples were then subjected to a neutral salt spray test as defined in ASTM B117. The samples were evaluated according to the two part method described
20 in ASTM D1654. Under part B of this method, which deals with general corrosion, the samples which were not coloured failed after about 500 hours, whereas those which were coloured were in most cases still passing after 1,034 hours.

- **Example 8**

25 An acid dye, CI Acid Blue 62, was prepared as follows:

* Lactic acid 2%

* CI Acid Blue 62 (Everacid TM Blue RRL) - 1%

* The dye bath was heated to 70°C and an anodised magnesium substrate on magnesium alloy AZ31 was introduced to it for two minutes after which time a wash
30 resistant stain was formed without degradation of the surface film.

- **Example 9**

A tube composed of Melram® 072 TS alloy (magnesium containing 12% silicon carbide in a mixed metal composite) was anodised by the procedure described in PCT/NZ96/00016 to a thickness of about $5\mu\text{m}$. This was then coloured yellow using
5 a vinyl sulphone reactive dye, Eversol® Yellow, at 60°C for 30 minutes, at a concentration of 0.5% with a concentration of 0.5% sodium carbonate and 0.25% sodium hydroxide. The result was a bright yellow-gold colour.

- **Example 10**

10 A sample of hot rolled magnesium alloy AZ31 sheet was anodised to a thickness of $15\mu\text{m}$ and coloured using a vinyl sulphone reactive dye, Eversol® Blue, at a concentration of 0.5%, together with 0.5% sodium carbonate and 1% sodium hydroxide, yielding a dark blue colouration of the sample.

WHAT WE CLAIM IS:

1. A method of colouring a magnesium or magnesium alloy article, said method comprising or including the steps of ensuring the article has, or providing the article with an anodized or other oxidised surface of the magnesium or magnesium alloy, and
5 contacting said anodized or other oxidised surface with at least one species of chromophoric moiety in a liquid carrier in conditions, or in a sequence of conditions, not substantially prejudicial to the integrity of said anodized or other oxidised surface yet which results in the chromophore(s) becoming associated (directly or via a moiety or species attached to the chromophore) with the surface by a reaction or adsorption.
- 10 2. A method of any one of claims 1 to 5 wherein said conditions exclude the prospect of an aluminium build up on said surface even should the magnesium have been alloyed with aluminium.
3. A method of claim 1 or 2 wherein the carrier is aqueous.
4. A method of any one of the preceding claims wherein said surface is anodized.
- 15 5. A method of any one of claims 1 to 5 wherein said surface is chemically oxidised.
6. A method of any one of the preceding claims wherein the conditions include elevated temperature(s).
7. A method of any one of the preceding claims wherein the step of contacting is
20 by immersion.
8. A method of any one of the preceding claims which includes washing the anodized or other oxidised surface prior to contact with said at least one species of chromophoric moiety in a liquid carrier.
9. A method of any one of the preceding claims which includes a washing step
25 subsequent to the contact with said at least one chromophoric moiety in a liquid carrier.
10. A method of claim 3 wherein said conditions involves a near neutral, neutral or alkaline pH.
11. A method of claim 3 wherein said pH is alkaline.
12. A method of any one of the preceding claims wherein said species is selected
30 from the group consisting of reactive dyes, direct dyes, VAT dyes, sulphur dyes and disperse dyes.

13. A method of any one of the preceding claims wherein said species is selected from the group consisting of vinyl sulphones, monochloro triazines, dichloro triazines, pyrimidines, phthalocyanines, quinoxalines, aniline derivatives, monofluoro triazines, anthraquinones, indigo and halogenated indigo derivatives, polysulphides, and diazo phenols.
14. A method of any one of claims 1 to 9 which includes
- (i) providing a bath containing a sulphur textile dye together with alkali and a reducing agent such that the dye is present in its water-soluble reduced leuco form;
- 10 (ii) immersing said article in said bath; and
- (iii) subsequently immersing said article in an oxidising solution to form the dye on its surface.
15. A method of claim 14 wherein said immersion in said bath is at approximately 90°C for approximately ½ an hour.
- 15 16. A method of claim 14 or 15 wherein said sulphur textile dye is provided at approximately double the normal concentration employed for textile dyeing.
17. A method of any one of claims 1 to 9 which comprises or includes
- (i) providing a bath containing a VAT textile dye together with an alkali and reducing agent such that the dye is present in its water soluble leuco form;
- 20 (ii) immersing said article in said bath; and
- (iii) immersing said article in a mildly acidic oxidising solution to form the dye on the surface of the article.
18. A method of claim 17 wherein said reducing agent is sodium dithionite.
19. A method of claim 17 or 18 wherein said article is immersed at approximately
- 25 70°C for approximately 30 minutes.
20. A method of any one of claims 17 to 19 wherein said VAT textile dye is provided at double the normal concentration employed for textile dyeing.
21. A method of any one of claims 17 to 20 wherein said article is immersed in said mildly acidic oxidising solution for approximately five minutes.
- 30 22. A method of any one of claims 1 to 9 which comprises or includes
- (i) providing a bath containing a vinyl sulphone reactive textile dye;

- (ii) immersing said article in said bath; and
 - (iii) washing said article.
23. A method of claim 22 wherein said bath is provided at a pH of approximately 12 and said article is immersed for approximately 30 minutes at approximately 60°C.
- 5 24. A method of claim 22 or 23 wherein said bath contains a reactive dye, and at least one of sodium carbonate, sodium hydroxide or sodium silicate.
25. A method of any one of claims 22 to 24 wherein said bath comprises a reactive dye in a concentration of 5g/L and sodium hydroxide at a sufficient concentration to raise the pH to about 12.
- 10 26. A method of any one of claims 22 to 25 wherein said dye contains a vinyl sulphone and amine functional groups.
27. A method of any one of claims 22 to 26 wherein said washing is in water at 60°C.
1. A method of claim 27 wherein the washing water includes a wetting agent.
- 15 29. A method of any one of claims 1 to 9 which comprises or includes
- (i) providing a bath containing a monochloro triazine reactive textile dye;
 - (ii) immersing said article in said bath; and
 - (iii) washing said article.
30. A method of claim 29 wherein was bath and said article is immersed for
- 20 approximately 30 minutes at approximately 60°C.
31. A method of claim 29 or 30 wherein said bath contains a reactive dye, and at least one sodium sulphate, sodium chloride, carbonate and sodium hydroxide.
32. A method of claim 31 wherein said bath comprises a reactive dye in a concentration of 0.5 - 2% w/v and Na_2SO_4 concentration is equal to dye concentration,
- 25 sodium carbonate 0.5 - 1% w/v and NaOH 0.25% w/v.
33. A method of any one of claims 29 to 32 wherein said washing is in water at about 80°C.
34. A method of claim 1 wherein said surface is anodized and said at least one species of chromophoric moiety in a liquid carrier is a reactive dye of a kind having a
- 30 vinyl sulphone functional group and wherein the conditions are within a temperature range of from 30 to 100°C during an immersion or spray presentation of the liquid dye

composition to the anodized surface for at least 10 minutes and thereafter a rinsing step with water at an elevated temperature.

35. A method as claimed in claim 34 wherein said contact time is about 30 minutes.
36. A method as claimed in claim 34 or 35 wherein said rinsing step is with hot
5 water containing a wetting agent and the temperature of the aqueous rinsing composition is 80°C or greater.
37. A method as claimed in any one of claims 34 to 36 wherein said temperature of the immersion or spraying with the liquid dye composition is at about 60°C.
38. A method as claimed in any one of claims 34 to 37 wherein the dye has a
10 concentration of at least about 0.5% w/v in an aqueous system.
39. A method as claimed in claim 1 wherein said surface is anodized and wherein the at least one species of chromophoric moiety in a liquid carrier is a reactive dye of a kind having a monofluoro triazine functional group and the conditions during the contact by immersion or spraying is at an elevated temperature.
- 15 40. A method as claimed in claim 39 wherein the contact time is for a period of from 30 to 60 minutes.
41. A method as claimed in claim 39 or 40 wherein the temperature of the contact is at about 70°C or higher.
42. A method as claimed in any one of claims 39 to 41 wherein the dye
20 concentration is from 0.5% to 2% w/v.
43. A method as claimed in claim 42 wherein there is also present sodium sulphate at substantially equal concentration to the dye, sodium carbonate at 0.5 to 1.0% w/v and sodium hydroxide to a concentration of about 0.25% w/v.
44. A method of any one of claims 39 to 43 wherein there is a rinsing step with hot
25 water containing a wetting agent and at a temperature of 80°C or greater.
45. A method of claim 1 wherein said at least one species of chromophoric moiety in a liquid carrier is that of a reactive dye having a functional group selected from the dichloro triazine, monofluoro triazine and difluoro triazine functions groups.
46. A method as claimed in claim 1 wherein at least one species of chromophoric
30 moiety in a liquid carrier is that of a reactive dye of the pyrimidine type.
47. A method of any one of claims 1 to 9 wherein at least one species of

chromophoric moiety in a liquid carrier is that of a vat dye.

48. A method of claim 47 wherein the dye is an anthraquinone or indigo derivative.

49. A method of claim 47 or 48 wherein the vat dye is dispersed in water and reduced to water soluble leuco form using a combination of a reducing agent and alkali.

5 50. A method of any one of claims 47 to 49 wherein said leuco dye is used to colour the anodized magnesium article by immersion or spraying.

51. A method of any one of claims 47 to 50 wherein the temperature of leuco dye is elevated.

52. A method of any one of claims 47 to 51 wherein the temperature of the leuco dye
10 is 60°C or higher.

53. A method of any one of claims 47 to 52 wherein the pH of leuco dye is 11.5 or greater.

54. A method of any one of claims 47 to 53 wherein the leuco dye dyed article is rinsed in cold water and then oxidised so that leuco dye is converted to insoluble
15 pigment.

55. A method of any one of claims 1 to 9 wherein the at least one species of chromophoric moiety in a liquid carrier is that of a sulphur dye.

56. A method of claim 55 wherein the moiety is attached to a polysulphide.

57. A method of claim 55 or 56 wherein the sulphur dye is dispersed in water and
20 reduced to water soluble leuco form (thiol form) using a combination of a reducing agent and alkali.

58. A method of any one of claims 55 to 57 wherein said leuco dye is used to colour anodized magnesium article by immersion or spraying.

59. A method of any one of claims 55 to 58 wherein the temperature of leuco dye is
25 elevated.

60. A method of any one of claims 55 to 59 wherein the dye is at 60°C or higher.

61. A method of any one of claims 55 to 60 wherein pH of the leuco dye is 11.5 or greater.

62. A method of any one of claims 55 to 61 wherein the leuco dye dyed article is
30 rinsed in cold water and then oxidised so that leuco dye is converted to insoluble pigment.

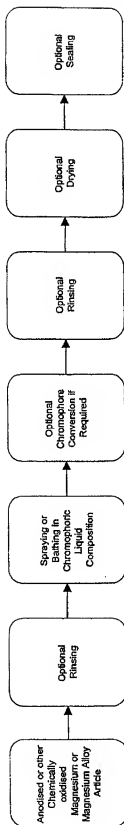
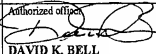


FIGURE 1

INTERNATIONAL SEARCH REPORT

International Application No.
PCT/NZ 98/00039

A. CLASSIFICATION OF SUBJECT MATTER		
Int Cl ⁶ : C25D 011/30		
According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED		
Minimum documentation searched (classification system followed by classification symbols) IPC6: C25D 011/30, 011/02, 011/00 C23C 022/84		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) DERWENT:IPC6 AS ABOVE+MAGNESIUM+MG		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4551211 A (KOBAYASHI et al.) 5 November 1985 Whole document	1-82
X	Derwent Abstract Accession No. 87-131552/19 JP 62-070600 A (UBE INDUSTRIES KK) 1 April 1987 Abstract	1-12, 82
A	Derwent Abstract Accession No. 52326C/30 JP 55-076094 A (SHOKOSHA KK) 7 June 1980 Abstract	
<input checked="" type="checkbox"/> Further documents are listed in the continuation of Box C <input checked="" type="checkbox"/> See patent family annex		
* Special categories of cited documents:	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention	
"A" document defining the general state of the art which is not considered to be of particular relevance	"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone	
"B" earlier document but published on or after the international filing date	"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art	
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"Z" document member of the same patent family	
"O" document referring to an oral disclosure, use, exhibition or other means		
"P" document published prior to the international filing date but later than the priority date claimed		
Date of the actual completion of the international search 22 May 1998	Date of mailing of the international search report 28 MAY 1998	
Name and mailing address of the ISA/AU AUSTRALIAN PATENT OFFICE PO BOX 200 WODEN ACT 2606 AUSTRALIA Facsimile No.: (02) 6285 3929	Authorized officer  DAVID K. BELL Telephone No.: (02) 6283 2309	

INTERNATIONAL SEARCH REPORT

International Application No.

PCT/NZ 98/00039

C (Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 4978432 A (SCHMELING et al) 18 December 1990 Whole document	
A	US 4976830 A (SCHMELING et al) 11 December 1990 Whole document	

INTERNATIONAL SEARCH REPORT
Information on patent family members

International Application No.
PCT/NZ 98/00039

This Annex lists the known "A" publication level patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent Document Cited in Search Report				Patent Family Member			
US	4551211	DE	3426666	JP	60024398	JP	60039198
		JP	63042720				
US	4978432	DE	3808609	EP	333048	JP	1301888
US	4976830	DE	3808610	EP	333049	JP	1301889
END OF ANNEX							